

THE ACTION OF  
THIONYL CHLORIDE  
AND OF  
PHOSPHORUS PENTACHLORIDE  
ON THE  
METHYLENE ETHERS  
OF  
CATECHOL DERIVATIVES

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LII.—*The Action of Thionyl Chloride and of Phosphorus Pentachloride on the Methylene Ethers of Catechol Derivatives.*

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THE synthesis of compounds containing an ortho-dihydroxybenzene nucleus is generally attended with difficulty owing to the instability of this nucleus. On the other hand, the methylene ethers of many such compounds are easily obtainable from piperonal, which substance, like benzaldehyde, readily undergoes a variety of reactions. The transformation of the methylene ethers into the phenolic compounds presents, however, considerable difficulty. Although the methylene group is somewhat more easily removed than methyl groups, the usual reagents for the preparation of phenolic compounds from the corresponding alkyl ethers generally bring about the disruption of

the molecule, when applied to catechol derivatives. One of the few examples of the successful application of such reagents is the preparation of protocatechualdehyde from piperonal by heating with dilute hydrochloric acid or with acid salts to 150—190° (D.R.-P. 16784 of 1904).

A peculiar reaction of the methylene ethers of catechol derivatives was discovered long ago by Fittig and Remsen (*Annalen*, 1871, 159, 114), and applied by them to piperonal and to piperonylic acid. By heating the former substance with phosphorus pentachloride, they obtained a tetrachloro-derivative, which undoubtedly has the constitution  $\text{Cl}_2:\text{C}:\text{O}_2:\text{C}_6\text{H}_3\cdot\text{CHCl}_2$ . By treatment with cold water, two chlorine atoms are replaced by an oxygen atom, and, according to Fittig and Remsen, this substance, termed dichloropiperonal, has the constitution  $\text{Cl}_2:\text{C}:\text{O}_2:\text{C}_6\text{H}_3\cdot\text{CHO}$ . By boiling water it is hydrolysed to carbon dioxide, hydrochloric acid, and protocatechualdehyde.

Recently, Pauly (*Ber.*, 1907, 40, 3096) has examined this reaction more closely, and described an interesting intermediate compound. He, for the first time, obtained dichloropiperonal quite pure (by distillation under reduced pressure) and was further able to replace the remaining pair of chlorine atoms of this substance by an oxygen atom (by heating with anhydrous oxalic acid, and by other means). Pauly thus obtained the cyclic carbonate of protocatechualdehyde,  $\text{CHO}\cdot\text{C}_6\text{H}_3\langle\text{O}\rangle\text{CO}$ . When boiled with water, this substance breaks up into carbon dioxide and protocatechualdehyde, and, for this reason, escaped the notice of Fittig and Remsen.

With the view of preparing other catechol compounds from the corresponding methylene ethers, the author was led to investigate the action of thionyl chloride, in consideration of the fact that the latter substance has often shown itself superior to phosphorus pentachloride in the preparation of acid chlorides. In a preliminary experiment, thionyl chloride was caused to act on piperonal. Up to 150°, scarcely any action took place, but at 180° an almost quantitative yield of "dichloropiperonal" was obtained on removal of the excess of thionyl chloride employed. The effect of heating with thionyl chloride was therefore the same as heating with phosphorus pentachloride, and subsequent treatment with cold water. When substances containing two catechol nuclei were employed, such as piperonyloin, some difficulty was at first experienced in interpreting the reaction. By heating with thionyl chloride, piperonyloin yielded a substance containing only two chlorine atoms. Since boiling water converted the dichloro-compound into a substance with two free catechol nuclei,\* both methylene groups had been attacked (as, indeed, one might

\* An account of these and similar substances will be published later.

expect). On Fittig and Remsen's view, the substance should therefore have contained four chlorine atoms, and the question arose whether "dichloropiperonal" is not in reality the cyclic carbonate of piperonylidene chloride, and whether it should not be formulated as



instead of  $\text{Cl}_2:\text{C} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{C}_6\text{H}_3 \cdot \text{CHO}$ , as supposed by Fittig and Remsen (and also by Pauly). Further experiments seem to leave no doubt that the former constitution is the correct one. That thionyl chloride, or phosphorus pentachloride and cold water, transforms methylene ethers of catechol derivatives into the corresponding cyclic carbonates was proved by their action on methylenedioxybenzene itself, and on piperonylic acid. Phosphorus pentachloride converts methylenedioxybenzene into a chloro-derivative of the probable constitution  $\text{Cl}_2:\text{C} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{C}_6\text{H}_4$ , and this is changed by cold water to a chlorine-free substance, the cyclic carbonate of catechol,  $\text{O}:\text{C} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{C}_6\text{H}_4$ , which has already been prepared by the action of carbonyl chloride on the sodium derivative of catechol.

The action of phosphorus pentachloride on piperonylic acid has already been investigated by Fittig and Remsen. According to these authors, cold water converts the crude liquid product of the reaction into a solid chloro-acid, to which they assigned the constitution  $\text{Cl}_2:\text{C}:\text{O}_2:\text{C}_6\text{H}_3 \cdot \text{CO}_2\text{H}$ . Since the chlorine content of the (somewhat impure) preparation corresponded more closely with one atom of chlorine only, they suggested that a further change takes place under the influence of cold water, resulting in a substance of the constitution  $\text{HO} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{C} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{C}_6\text{H}_3 \cdot \text{CO}_2\text{H}$ , but owing to the poor agreement of their analytical results with the calculated values, they did not attach much importance to this suggestion. The explanation is now, however, obvious. The supposed chloro-acid was in reality the cyclic carbonate of protocatechuoyl chloride,  $\text{O}:\text{C} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{C}_6\text{H}_3 \cdot \text{COCl}$ , and the carbon and hydrogen content found by Fittig and Remsen agrees closely with that required by the above formula :

Found (by Fittig and Remsen), C = 48.43 ; H = 2.01.

$\text{C}_8\text{H}_3\text{O}_4\text{Cl}$  requires C = 48.36 ; H = 1.51 per cent.

The chlorine found by them was somewhat low, 16.81 instead of 17.88 per cent., as might have been expected after treatment of an acid chloride with water.

The behaviour of the substance towards hydroxyl and amino-groups

agrees in every respect with that of an aromatic acid chloride, and leaves no doubt as to its constitution. It has been employed in the synthesis of new catechol derivatives, a number of which are described below.

In accordance with what has been said above, the carbonate of protocatechuoyl chloride should be produced directly from piperonylic acid by the action of thionyl chloride at 180°, and this was indeed found to be the case. On removal of the excess of thionyl chloride in a vacuum, the acid chloride remains behind as a crystalline mass, and it was in this experiment that its true nature was first recognised.

The direct production of cyclic carbonates by successive treatment of methylene ethers with phosphorus pentachloride and with cold water has already been observed by Delange (*Compt. rend.*, 1904, 138, 423 and 1701) who obtained in this way the cyclic carbonates of 3:4-dihydroxy-1-ethyl-, -*α*-1-propyl-, and -1-isopropyl-benzene.

It seems safe to conclude from the above evidence that the two chlorine atoms which are introduced by phosphorus pentachloride into the methylene group are much more labile than any other chlorine atoms which may be introduced at the same time into another part of the molecule. By cold water, moist air, anhydrous formic acid, glacial acetic acid, or acetic anhydride (Delange) they are replaced by an oxygen atom; thionyl chloride introduces this oxygen atom at the outset. The violence with which these two chlorine atoms react with hydroxyl- and amino-groups is without parallel among aromatic chloro-compounds, although not surprising if we regard the substances in question as the dichlorides of an ethereal salt of orthoformic acid. If we consider that benzylidene chloride requires heating with water to 140—160° in order to convert it into benzaldehyde, we should not expect the carbonate of dihydroxybenzylidene chloride to react with cold water. The two chlorine atoms, which Pauly replaced by an oxygen atom in the production of protocatechualdehyde carbonate, are therefore those of the aldehyde group and not, as he seems to imagine, those in the carbonyl (methylene) group.

#### EXPERIMENTAL.

##### *Conversion of Methylenedioxybenzene into Carbonyldioxybenzene.*

1.45 Grams of crude methylenedioxybenzene, b. p. 170—180°, containing a little methylene iodide, and obtained by the action of methylene iodide on disodium catechol (Mouren, *Bull. Soc. chim.*, 1896, [iii], 15, 655) were heated for half an hour under a reflux condenser with 3.5 grams (2 mols.) of phosphorus pentachloride.

After removal of the phosphorus trichloride by distillation at atmospheric pressure, the dichloromethylenedioxybenzene,  $\text{Cl}_2 \cdot \text{CO}_2 \cdot \text{C}_6\text{H}_4$ , distilled in a vacuum at about  $90^\circ$ . On treating the distillate with cold water, hydrogen chloride was evolved and 0.75 gram of a white, chlorine-free solid resulted, which, when crystallised from benzene, melted at  $119^\circ$ . The melting point was not changed by mixing with a specimen of carbonyldioxybenzene (obtained by means of carbonyl chloride). The latter specimen melted at  $119.5^\circ$ .

*Action of Thionyl Chloride on Piperonyl Alcohol.*

Two grams of piperonyl alcohol\* were dissolved in 6 c.c. of thionyl chloride; an energetic reaction took place at once (formation of piperonyl chloride), and the solution was then heated in a sealed tube to  $180^\circ$  for seven hours. After removal of the excess of thionyl chloride, the product of the reaction distilled at  $165\text{--}183^\circ/12$  mm. On boiling the distillate with formic acid, a more than 50 per cent. yield of 3:4-carbonyldioxybenzoic acid was obtained. The piperonyl chloride had therefore been oxidised to carbonyldioxybenzoyl chloride,



(b. p.  $166\text{--}167^\circ/13$  mm.).

The action of thionyl chloride on benzyl alcohol at  $180^\circ$  was next examined, and found to be completely analogous. The product of the reaction was evidently a mixture of benzyl and benzoyl chlorides, and the highest fraction, boiling at  $198^\circ$ , yielded benzoic acid.

Phosphorus pentachloride acting on piperonyl alcohol produced a tar from which nothing could be isolated.

*3:4-Carbonyldioxybenzoyl Chloride,  $\text{O}:\text{C}:\text{O}_2:\text{C}_6\text{H}_3:\text{COCl}$ .*

Piperonylic acid heated with an excess of thionyl chloride on the water-bath furnishes piperonyl chloride, melting at  $80^\circ$ , and boiling at  $140\text{--}141^\circ/8$  mm., which has already been prepared by Perkin and Robinson (*Proc.*, 1905, 21, 287) by means of phosphorus trichloride. At a higher temperature, thionyl chloride forms 3:4-carbonyldioxybenzoyl chloride, the methylene group being also attacked.

Two grams of piperonylic acid were heated with 6 c.c. of thionyl chloride to  $180\text{--}200^\circ$  for eight hours. On distilling off the excess

\* The piperonyl alcohol and piperonylic acid employed in these experiments were prepared from piperonal by Cannizzaro's reaction. Aqueous potassium hydroxide was found to be much better than alcoholic, as used by Decker and Koch (*Ber.*, 1905, 39, 1741), since it gave a larger yield of a purer product. Fifty-six grams of piperonal, mixed with 36 grams of potassium hydroxide dissolved in 24 grams of water, gave, after standing 24 hours at the laboratory temperature, 28 grams of the acid and 22 grams of the alcohol (m. p.  $52\text{--}53^\circ$ ).

of thionyl chloride in a vacuum on the water-bath, a pale brown, viscous liquid remained, which crystallised on cooling, and distilled at 166—167°/12 mm. On crystallisation from a mixture of benzene and light petroleum, it melted at 68°:

0.1828 gave 0.3278 CO<sub>2</sub> and 0.0276 H<sub>2</sub>O. C = 48.5; H = 1.7.

0.1483 „ 0.1044 AgCl (by boiling with water). Cl = 17.4.

C<sub>8</sub>H<sub>3</sub>O<sub>4</sub>Cl requires C = 48.4; H = 1.5; Cl = 17.9 per cent.

The compound was also prepared by heating piperonylic acid with three molecular proportions of phosphorus pentachloride under a reflux condenser for several hours, and gradually distilling off the phosphorus trichloride and phosphoryl chloride through a fractionating column, so that the temperature of the residual liquid at last rose to 160°. On distillation, a little phosphorus pentachloride sublimed, and then the product of the reaction distilled at 149—150°/12 mm. It was not quite pure, as the reaction was incomplete, some unchanged piperonyl chloride being present. (Found: Cl = 39.2; C<sub>8</sub>H<sub>3</sub>O<sub>3</sub>Cl<sub>3</sub> requires Cl = 42.0 per cent.)

After the substance had been freed from phosphorus halides, it no longer reacted readily with cold water, on account of its insolubility, and it was not found possible to convert it easily into a solid product by Fittig and Remsen's method. When dissolved in acetone, it reacted violently with water, so that the acetone was raised to its boiling point. The most convenient method of transformation into 3:4-carbonyldioxybenzoyl chloride was found to be prolonged exposure in a thin layer to moist air, when in the course of one or two days the substance was completely transformed into a hard, crystalline mass, which, when recrystallised from benzene and light petroleum, was found to be identical with the substance obtained by thionyl chloride direct.

The constitution of the substance is proved by its transformation to 3:4-carbonyldioxybenzoic acid and its derivatives; all these substances can be further changed to the corresponding derivatives of protocatechuic acid by boiling with water.

*3:4-Carbonyldioxybenzoic Acid*, O:C:O<sub>2</sub>:C<sub>6</sub>H<sub>3</sub>:CO<sub>2</sub>H.

When 3:4-carbonyldioxybenzoyl chloride is heated with a little anhydrous formic acid, it readily dissolves, but soon an energetic reaction begins; hydrogen chloride is evolved and 3:4-carbonyldioxybenzoic acid separates. By using enough formic acid to keep the substance in solution and boiling for a short time, the latter at once crystallises out in a condition of analytical purity. Glacial acetic acid may be used instead of formic acid, and dichloropiperonyl chloride may be employed instead of carbonyldioxybenzoyl chloride:



0.1687 gave 0.3289  $\text{CO}_2$  and 0.0365  $\text{H}_2\text{O}$ .  $\text{C} = 53.2$ ;  $\text{H} = 2.4$ .

$\text{C}_8\text{H}_4\text{O}_5$  requires  $\text{C} = 53.3$ ;  $\text{H} = 2.2$  per cent.

3 : 4-Carbonyldioxybenzoic acid melts at  $228^\circ$  with effervescence. It is insoluble in water, and somewhat sparingly soluble in most organic solvents in the cold. Its alcoholic solution is not coloured by ferric chloride. On boiling the acid with water or with salt solution, it is quantitatively converted into protocatechuic acid, which separates in white crystals melting at  $197\text{--}198^\circ$ .

*Methyl 3 : 4-Carbonyldioxybenzoate*,  $\text{O}:\text{C}:\text{O}_2:\text{C}_6\text{H}_3\cdot\text{CO}_2\cdot\text{CH}_3$ .

This substance was prepared by dissolving the acid chloride in methyl alcohol without rise of temperature. On the addition of water, crystals separated melting at  $90^\circ$  :

0.1752 gave 0.3549  $\text{CO}_2$  and 0.0495  $\text{H}_2\text{O}$ .  $\text{C} = 55.4$ ;  $\text{H} = 3.1$ .

$\text{C}_9\text{H}_6\text{O}_5$  requires  $\text{C} = 55.7$ ;  $\text{H} = 3.2$  per cent.

*Methyl 3 : 4-carbonyldioxybenzoate* is very soluble in most organic solvents, and does not give a reaction with ferric chloride. By boiling with water or making alkaline with ammonia, it is changed to methyl protocatechuate, which could, however, not be obtained quite pure owing to further decomposition, resulting in the formation of protocatechuic acid.

*Phenyl-3 : 4-carbonyldioxybenzoate*,  $\text{O}:\text{C}:\text{O}_2:\text{C}_6\text{H}_3\cdot\text{CO}_2\cdot\text{C}_6\text{H}_5$ .

Equimolecular proportions of phenol and of 3 : 4-carbonyldioxybenzoyl chloride were heated together, until the evolution of hydrogen chloride ceased. A little benzeno was then added to the hot liquid and, on cooling, *phenyl 3 : 4-carbonyldioxybenzoate* crystallised in stout crystals, melting at  $126^\circ$  :

0.1433 gave 0.3458  $\text{CO}_2$  and 0.0405  $\text{H}_2\text{O}$ .  $\text{C} = 65.8$ ;  $\text{H} = 3.1$ .

$\text{C}_{14}\text{H}_8\text{O}_5$  requires  $\text{C} = 65.6$ ;  $\text{H} = 3.1$  per cent.

*Phenyl Protocatechuate*,  $(\text{OH})_2\text{C}_6\text{H}_3\cdot\text{CO}_2\cdot\text{C}_6\text{H}_5$ .

The substance just described was suspended in boiling water, and dilute ammonia was added drop by drop until all was dissolved. If an excess is avoided, the solution scarcely darkens at all. After filtration, dilute hydrochloric acid was added drop by drop to the hot solution, so that crystals of phenyl protocatechuate separated out. The substance was recrystallised from very dilute alcohol and then melted at  $189^\circ$ . It is readily soluble in cold alcohol, but almost

insoluble in boiling water; its solution is coloured green by ferric chloride:

0.1090 gave 0.2717 CO<sub>2</sub> and 0.0438 H<sub>2</sub>O. C = 68.0; H = 4.5.

C<sub>13</sub>H<sub>10</sub>O<sub>14</sub> requires C = 67.8; H = 4.4 per cent.

*Methoxyphenyl 3:4-Carbonyldioxybenzoate,*



Prepared like the phenyl derivative from the acid chloride and guaiacol, this substance yielded stout crystals, sparingly soluble in hot benzene and melting at 159°:

0.1402 gave 0.3255 CO<sub>2</sub> and 0.0442 H<sub>2</sub>O. C = 63.3; H = 3.5.

C<sub>15</sub>H<sub>10</sub>O<sub>6</sub> requires C = 62.9; H = 3.5 per cent.

*Methoxyphenyl Protocatechuate, (OH)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·CO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·O·CH<sub>3</sub>.*

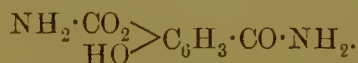
Prepared from the compound just described in the same way as the corresponding phenyl derivative, it yielded prisms melting at 194°:

0.1598 gave 0.3768 CO<sub>2</sub> and 0.0680 H<sub>2</sub>O. C = 64.3; H = 4.7.

C<sub>14</sub>H<sub>12</sub>O<sub>5</sub> requires C = 64.6; H = 4.6 per cent.

*Protocatechuamide, (OH)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>·CO·NH<sub>2</sub>.*

The preparation of this substance presented some difficulty owing to the instability of the carbonyl group towards ammonia. When 3:4-carbonyldioxybenzoyl chloride was treated with dry ammonium carbonate, a substance resulted which gave a green coloration with ferric chloride, and could not be obtained crystalline. By passing dry ammonia into the acid chloride dissolved in carefully dried benzene, a white, amorphous precipitate was immediately formed, which was collected and dried in a vacuum desiccator over paraffin wax and sulphuric acid. It was expected that the precipitate would consist of a mixture of ammonium chloride and 3:4-carbonyldioxybenzamide, and it was hoped that the former substance could be extracted by water. Almost the whole of the precipitate dissolved, however; on prolonged standing crystals separated. These were recrystallised from ethyl acetate, in which they were but sparingly soluble, and they then melted at 131° with effervescence. The new substance was probably a *urethane* of protocatechuic acid, having the formula:



0.1088 gave 12.3 c.c. moist nitrogen at 15.5° and 764 mm. N = 13.3.

C<sub>8</sub>H<sub>8</sub>O<sub>4</sub>N<sub>2</sub> requires N = 14.3 per cent.

*Protocatechuamide* was, however, obtained by keeping 3:4-carbonyldioxybenzoyl chloride with an excess of dry liquid ammonia in a sealed

tube at the laboratory temperature for two days. On allowing the excess of ammonia to evaporate at the ordinary temperature, a red solid remained, which was completely freed from ammonia in a vacuum over sulphuric acid and then crystallised from water.

The crystals were somewhat coloured and melted at  $212^{\circ}$ . With ferric chloride they gave an intense green coloration :

0.2392 gave 18.7 c.c. moist nitrogen at  $5^{\circ}$  and 770 mm.  $N = 9.7$ .

$C_7H_7O_3N$  requires  $N = 9.2$  per cent.

3 : 4-Carbonyldioxybenzanilide,  $O:C:O_2C_6H_3 \cdot CO \cdot NH \cdot C_6H_5$ .

Two molecular proportions of aniline, dissolved in a little benzene, were added to 0.5 gram of 3 : 4-carbonyldioxybenzoyl chloride, dissolved in 10 c.c. of benzene. A precipitate consisting of the anilide and of aniline hydrochloride was formed. On extracting the precipitate with water, the anilide remained behind and was then crystallised from boiling alcohol and subsequently from ethyl acetate. It formed white, hair-like needles melting sharply at  $214^{\circ}$  :

0.2271 gave 11.0 c.c. moist nitrogen at  $14^{\circ}$  and 766 mm.  $N = 5.7$ .

$C_{14}H_9O_4N$  requires  $N = 5.5$  per cent.

Protocatechuanilide,  $(OH)_2C_6H_3 \cdot CO \cdot NH \cdot C_6H_5$ .

3 : 4-Carbonyldioxybenzanilide was dissolved in pyridine and an equal volume of water was then added; bubbles of carbon dioxide were given off. After removal of most of the pyridine by distillation, white, glistening plates separated, consisting of protocatechuanilide. The hydrolysis of the carbonate can also be performed by suspending it in boiling water, and adding dilute ammonia, drop by drop, as described for phenyl protocatechuate. The substance retains water at  $100^{\circ}$  and was dried at  $115^{\circ}$  until of constant weight :

0.1441 gave 0.3591  $CO_2$  and 0.0606  $H_2O$ .  $C = 68.0$  ;  $H = 4.7$ .

0.3177 ,, 16.6 c.c. moist nitrogen at  $14^{\circ}$  and 766 mm.  $N = 6.2$ .

$C_{13}H_{11}O_3N$  requires  $C = 68.1$  ;  $H = 4.8$  ;  $N = 6.1$  per cent.

Protocatechuanilide melts at  $166-167^{\circ}$ . It is sparingly soluble in hot water, but readily so in hot alcohol; its solutions gave the characteristic green coloration with ferric chloride. The substance has been prepared before from protocatechuic acid by Schiff (*Ber.*, 1882, 15, 2589) and by Thibault (*Bull. Soc. chim.*, 1904, [iii], 31, 920). The latter author criticises Schiff's method of preparation and himself gives the melting point  $154-156^{\circ}$ . The analytical figures and the melting point given above would, however, appear to refer to a purer specimen, and illustrate the advantage of pre-

paring catechol derivatives, when possible, from the corresponding methylene ethers by way of the cyclic carbonates.

*Action of Thionyl Chloride and of Phosphorus Pentachloride on Piperonal.*

Two grams of piperonal were heated with 8 c.c. of thionyl chloride to 220° for seven hours. On removal of the excess of thionyl chloride in a vacuum on the water-bath, a viscous liquid remained behind, which crystallised from benzene and light petroleum and was found to be 3:4-carbonyldioxybenzylidene chloride ("dichloropiperonal"). The yield was 60 per cent. The "dichloropiperonal dichloride" of Fittig and Remsen, formed by the action of phosphorus pentachloride on piperonal, was found to distil without decomposition at 152—153°/9 mm., but could, nevertheless, not be obtained quite pure. (Found, Cl=50·35;  $C_8H_4O_2Cl_4$  requires Cl=51·8 per cent.)

The impurity was probably a trace of unchanged piperonal dichloride. The tetrachloro-compound was obtained crystalline by cooling it in carbon dioxide and acetone, and was found to melt at 14—15°. It is very soluble in all organic solvents, including light petroleum. The two chlorine atoms of the methylene group are replaced by an oxygen atom through the action of anhydrous formic or acetic acid in the cold; on boiling, the second pair of chlorine atoms is removed, with the formation of Pauly's cyclic carbonate of protocatechualdehyde.

*Piperonal dichloride*, which was cursorily referred to by Fittig and Remsen, has now been obtained pure. When piperonal is mixed with one molecular proportion of phosphorus pentachloride, enough heat is developed to liquefy the mixture and almost complete the reaction. On distilling the phosphoryl chloride under atmospheric pressure, the residue left in the flask became dark blue and a certain amount of decomposition took place. Most of the substance, however, distilled constantly at 141°/8 mm. and at once crystallised in the receiver; the yield was 60 per cent. of the theoretical:

0·2024 gave 0·2796 AgCl. Cl = 34·2.

$C_8H_5O_2Cl_2$  requires Cl = 34·6 per cent.

Piperonal dichloride forms large, acicular crystals from a mixture of benzene with much light petroleum, and melts at 59°. It resembles the closely related carbonate of protocatechualdehyde dichloride ("dichloropiperonal" of Fittig and Remsen). Both substances are unstable in moist air and gradually turn blue, and both are readily converted into the corresponding aldehyde by boiling with formic acid. Piperonal dichloride was by this means reconverted into piperonal, melting at 37°

and boiling at  $133^{\circ}/8$  mm. When piperonal is heated with an excess of thionyl chloride on the water-bath, the same dichloride is slowly formed.

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